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IDENTIFICATION OF ORGANIC COMPOUNDS IN THE ATMOSPHERE

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ABSTRACT

This report describes a technique for concentrating traces of oxygenated organic compounds in air. The method depends upon the use of a 0.125 by 6-inch copper tube filled with an ordinary gas chromatographic column packing. When a sample of approximately 1000 ml of polluted air is pumped through the tube with a rubber aspirator bulb, a sufficient quantity of pollutants is absorbed for subsequent detection and identification by gas chromatography with a hydrogen flame detector. The limit of sensitivity is estimated to be about 5 ng/l. Application of the method to samples collected at 17 Birmingham locations resulted in the tentative identification of about 30 oxygenated organic compounds.

IDENTIFICATION OF ORGANIC COMPOUNDS IN THE ATMOSPHERE

I. INTRODUCTION

The primary objective of this work was the development of an improved method of sampling the atmosphere to make possible identification of oxygenated organic compounds that were expected to be present in concentrations below about 1 part per million. The approach was to investigate the use of packed columns similar to those used in gas chromatographic analysis. The packed columns (hereafter also referred to as sample loops) were to be shorter in length than the usual gas chromatographic columns. It was expected that sufficient quantities of organic compounds might be collected to permit subsequent desorption and analysis with the aid of sensitive gas chromatographic detectors, such as the hydrogen flame detector. It was also expected that individual compounds could be identified by gas chromatographic techniques, possibly with the aid of infrared and mass spectroscopy. The proposed method would make it possible to provide some degree of selective sampling by packing the sample loops with materials that would be retentive for the more polar substances but less retentive for the hydrocarbons that presumably constitute a major part of the organic substances in the atmosphere. Also, the problem of handling and separating relatively large quantities of water would not be serious.

Insofar as was known at the time the application for this grant was submitted, the proposed sampling technique had not previously been used. During the course of the investigation, several publications appeared that described the results of related investigations.[1-7] Because some of these investigations, notably that of Williams,[5] described sampling techniques similar to the one contemplated for this project, our original objectives were modified somewhat. Instead of placing primary emphasis on identification of specific compounds, we attempted to utilize the sampling technique to obtain patterns of composition characteristic of various locations within the urban Birmingham area. The procedure finally developed is described in Section III and the results are given in Section IV.

Another objective of this work was to examine possible relationships between the patterns of composition in a specific area and the incidence of lung disease in that area. However, since no characteristic patterns could be established, this objective was not realized.

II. PRELIMINARY EXPERIMENTAL WORK

Before the procedures, apparatus, and materials described in Section III were selected for the systematic analysis of air samples, various materials and techniques were evaluated in preliminary experiments.

A. Use of Charcoal as an Adsorbent

At the beginning of this project, several samples obtained by passing large volumes of air over activated charcoal had been collected by the Public Health Service staff then conducting an air-pollution survey in Birmingham. These samples had been collected at various sites in the city and county for the ultimate purpose of analyzing the adsorbed materials and, possibly, obtaining "fingerprints" characterizing specific localities with respect to the less abundant air pollutants. Although a purpose of our project was to try to develop a better sampling method, we undertook the examination of several of the charcoal samples. These samples typically consisted of about 200 g of activated charcoal through which some 50,000 to 70,000 cubic feet of air had been pumped at ambient temperatures.

For analysis, the sample was transferred to a flask and heated to 325°C over 1.5 hours at a pressure of 0.2 torr. The volatile substances were condensed in ice-salt and liquid nitrogen traps. Usually, about 50 ml of condensate was obtained. It consisted almost entirely of water, as expected. Plugging of the traps was a problem that was not satisfactorily resolved. The condensate was extracted with carbon tetrachloride and the extract was subjected to gas chromatographic analysis. In some instances, a portion of the aqueous condensate was injected directly into the sample port of a gas chromatograph. The analytical columns were selected for optimum separation of hydrocarbons from oxygenated compounds. Chromatograms with various numbers of peaks and peak patterns were obtained.

To obtain information about the general composition of the materials eluted from the charcoal, the technique of functional group analysis by syringe reactions as described by Hoff and Feit[8] was applied. In this technique, various functional group classification reactions are carried out by placing appropriate reagents in the syringe used to inject a sample into a gas chromatograph. The method permits the detection of various organic functional groups and the differentiation of classes of compounds. Preliminary experiments with known mixtures of oxygenated compounds in air with various functional groups demonstrated that the method was effective. However, when the

known mixtures were passed over activated charcoal, and the charcoal was heated under reduced pressure in the same manner that the atmospheric samples collected by the Public Health Service staff were treated, the compounds generally could not be detected in the condensate. In fact, other compounds that were not identified were evolved. The use of the syringe technique for examining the atmospheric samples collected on charcoal gave no indication that oxygenated compounds were present.

The several severe difficulties encountered in these experiments led to a decision to abandon efforts to analyze the materials adsorbed on charcoal. The experiments with known mixtures of oxygenated compounds confirmed the expectation that reactions occurring on charcoal would change the chemical nature of the original airborne substances. The extraction of traces of oxygenated compounds from large volumes of water was difficult, and there were, also, uncertainties about the relative affinity of charcoal for large amounts of water and small amounts of organic compounds.

B. Use of Short Packed Columns for Concentrating Organic Compounds from Air

1. The role of particulate materials and water vapor

Little information is available on the distribution of the more volatile oxygenated organic compounds in air between the vapor phase and the particulate phase. (We were primarily interested in compounds of relatively low molecular weight.) In our early work, we conducted experiments in which air was passed through retentive filters before it entered the sample loops. It was shown experimentally that, of several kinds of filter materials, glass-fiber filters were the least retentive for volatile organic compounds. No evidence was found to indicate that the use of a filter affected the quantity or nature of the substances retained by the sample loops; results were similar whether or not a particulate filter was used. It seems likely that most of the particles in the air contained very little volatile material or that they were small enough to pass through a 6-inch packed column without beirg stopped by impaction on the surtaces of the packing materials. Some work on the composition of the particulate materials indicated that most of them were considerably less volatile than the airborne compounds collected by the sampling loops. It was concluded that particulate filters were not needed in the sampling system.

The effect of the water vapor in the air on the sampling system was also studied. Two considerations made it seem unlikely that water vapor would cause trouble in the planned analyses: water would probably be strongly retained in the first section of the sampling loop; and, even if it desorbed from the sample loops along with the organic materials, it would not produce a significant signal in the hydrogen flame ionization detector. As with filters, some early experimental work was conducted with a tube containing anhydrous K_2CO_3 in the sampling line; the conclusions were reached that the K_2CO_3 had no important effect on the nature or quantity of the organic materials absorbed in the sample loops and that exclusion of water vapor from the sample loops was not necessary.

2. Design of sample loops

The factors affecting the design of the sample loop were: material of construction, shape, diameter, length, flow rate, temperature, pressure, and the equilibrium distribution of the compound to be absorbed between the gas phase and the stationary phase. Discussions of the theory of the method of concentration have been given by Cropper and Kaminsky[6] and by Novak, Vasak, and Janak.[7] When air containing a fixed concentration of a single compound is made to flow through a packed column, the stationary phase will retard the passage of the compound so that it moves behind an advancing front. The optimum time for sampling will be the time required for the front to travel to the exit end of the column. There should be a characteristic optimum sampling time for each compound in the air, and this optimum time should be related to the retention time of the compound on the column. Thus, the design of a sample loop for a mixture of compounds of unknown identity is necessarily arbitrary. One practical consideration is that the sample loop must retain sufficient amounts for subsequent detection.

An investigation was conducted to establish optimum characteristics for sample loops for retaining organic materials from air. A dilution apparatus was set up to give concentrations in air of 0.1 to 1.0 µg/l. of several low-molecular weight aldehydes, ketones, alcohols, and esters. The efficiencies of absorption of these compounds by sample loops of various types (and with various packings) were determined. After a measured volume of sample air containing a known concentration of compound had passed through a loop, the amount of absorbed compound was determined by gas chromatography. Although the results of these experiments were not reproducible and were not considered to be conclusive, they did help in choosing the length of the sample loops and the flow rate of air. As a result of these experiments, and especially of practical experience, the sample loops described in Section III.A. were used to obtain the data given in Section IV.

3. Selection of packing materials for sample loops

The most important properties desired in the packing materials for the sample loops were: strong affinity for oxygenated compounds; poor affinity for hydrocarbons; freedom from volatile materials; thermal stability; and inertness of the support. Since it was expected that the ratio of hydrocarbons to oxygenated compounds in the air passed through the loop would be high, a packing material that would effect a partial separation of these two classes of compounds was desirable. Thermal stability was necessary so that compounds retained in the sample loops could be desorbed without being contaminated by substances formed by decomposition of the packing material.

With the aid of the dilution apparatus described in Section II.B.2., known concentrations of several compounds (diethyl ether, acetone, 2-butanone, ethyl acetate, propionaldehyde, hexane, octane, and toluene) in air were passed into sampling loops containing various liquid substrates on inert supports. The times required for a compound to traverse the loop and appear at the exit end were noted. Also, the relative ease of desorption from the various packing materials was determined. On the basis of these experiments, Reoplex 400 (polypropylene glycol adipate, obtained from Applied Science Laboratories, State College, Pa.) appeared to be a satisfactory material for use in the sample loops. The general quality of the chromatograms obtained from air samples after desorption from Reoplex 400 was good, and this material was adopted for use in all subsequent work. The solid support used with the Reoplex 400 was 60- to 80-mesh, acid-washed, dimethylchlorosilane-treated Chromosorb W (a Johns-Manville product distributed by Applied Science Laboratories, State College, Pa.).

4. Design of system for transferring samples from the loops to analytical columns

To transfer the sample material from the loops to the gas chromatographic column for analysis, it was necessary to heat the loops to vaporize the absorbed material and to flush the vapor into the analytical column with helium. The first approach was to connect the loop to a gas-sampling valve (Model GV-11, Hewlett-Packard Co., Avondale, Pa.) and wrap the loop, valve, and connecting lines with heating tape; difficulties in changing loops and absorption of sample vapors by the "O" ring seals in the valve made this method unsatisfactory. Another approach was to place the loop inside the oven of the gas chromatograph and connect the ends of the loop to two externally-operated Teflon-sealed valves; this arrangement was unsatisfactory because the Teflon seals in these valves failed rapidly.

The most satisfactory system incorporated a double four-way valve (Model P5-418T, Circle Seal Corporation, Anaheim, Calif.) which was designed to operate at temperatures up to 200°C. Figure 1 illustrates the system employing this valve. The valve and the sample loop were housed in a small electrically heated oven (175°C) attached to the outside of the gas chromatograph oven. The valve was operated by an external handle to open the sample loop at both ends and flush the vapor content into the analytical column with helium. The resolution of the sample components on the analytical solumn was satisfactory. Tests with known compounds indicated that retention times were reasonably reproducible.

5. Selection of packing material for the analytical columns

The primary requirement for the analytical gas chromatographic column was that it should provide good resolution of peaks and minimum tailing. The choice of column packing material was based upon experimental evaluations of several materials: Carbowax 20M (Applied Science Laboratories, State College, Pa.), W-98 and LAC (Hewlett Packard Co., Avondale, Pa.), Porapak Q, or Porapak S (Waters Associates, Inc., Framingham, Mass.). The Porapak columns were used for analyses of most of the samples.

6. Use of infrared absorption and mass spectroscopy for identification

Several attempts were made to isolate column effluent fractions and to obtain their infrared absorption spectra. In no case were we able to obtain a sufficient quantity of sample for positive identification of the isolated fraction. Accumulation of fractions having the same retention time from several air samples was not practical because the compositions of the samples varied widely from time to time.

It was hoped that the Institute's acquisition of a high-resolution, double-focusing mass spectrometer at about the mid-point of the grant period would permit some identification work with this instrument. This type of mass spectrometer proved to be difficult to use for the purpose and no satisfactory results were obtained. Because of the time and effort that seemed to be required to get useful information from infrared and mass spectral methods, only gas chromatographic retention times were used for the analyses described in Section IV.

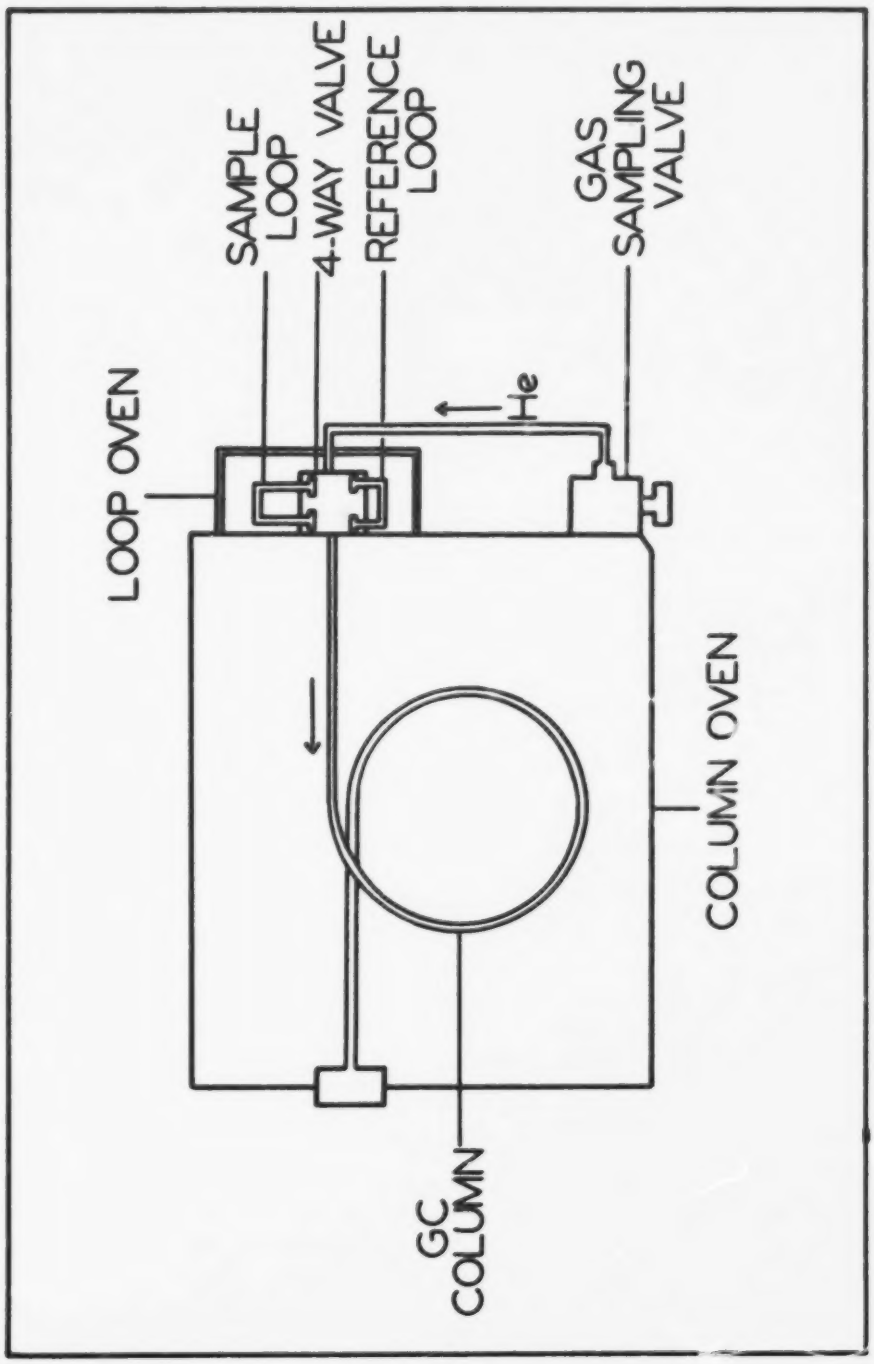

Figure 1. System for Transfer of Sample from Sample Loop to Gas Chromatograph Column

III. EXPERIMENTAL APPARATUS AND PROCEDURES

Following are descriptions of the special apparatus and procedures that were adopted for sampling and analyzing organic pollutants in air. The organic compounds were concentrated by drawing the air through sample loops, desorbed by heating the sample loops, and analyzed by passing the desorbed vapors through analytical gas chromatographic columns.

A. Sample Loops

Twenty-seven sample loops were prepared as follows: a 6-inch length of 0.25-inch tubing was bent into a U-shape. The ends were fitted with Swagelok nuts and ferrules. The loops were packed with 25% of Reoplex 400 (polypropylene glycol adipate) on 60- to 80-mesh acid-washed and silane-treated Chromosorb W). Before they were used for collecting samples, the loops were conditioned and freed of volatile materials by passing dry nitrogen through them at 200°C. The sample loops were capped until used and could be reconditioned for repeated use.

B. Procedure for Collecting Samples

At a sample collection site the loops were uncapped and connected to a rubber aspirator bulb. Air was pulled through the loops for 10 minutes by compressing and releasing the rubber bulbs several times. Approximately 1000 ml of air was pulled through each loop. The loops were then recapped. The absorbed sample was analyzed by gas chromatography, usually within a few hours but occasionally after two or three days.

C. Desorption

The sample loops were connected to the four-way valve which was mounted in a small, especially constructed, electrically heated oven. This oven was attached to the outside of the gas chromatograph oven and was usually at 175°C. The loop was held at the oven temperature for 5 minutes to permit desorption of sample vapors, and then the valve was opened to flush the sample vapor into the gas chromatographic column with helium. Figure 1 shows the arrangement of the sample loop, the valve, and the two ovens.

D. Gas Chromatographic Analysis

An F&M Model 5756A gas chromatograph (Hewlett-Packard Co., Avondale, Pa.) with a hydrogen flame detector was used. The analytical columns were made from 3 feet of 0.125-inch stainless

steel tubing packed with either Porapak Q or Porapak S. For a few analyses, Carbowax 20 M on Chromosorb W was used. The carrier gas was helium, flowing at 50 ml/min. At the beginning of the analysis the column-oven temperature was held at 130°C for 6 minutes; then the temperature was increased at the rate of 10 degrees/min until 200°C was reached. The temperature was held at 200°C for 5 minutes. The retention times for the recorded peaks were tabulated and compared with the retention times for a variety of known compounds for tentative identification.

IV. RESULTS AND DISCUSSION

During the late winter and early spring of 1968, approximately 55 samples were collected at 17 sites in Birmingham. The sites included some near foundries, chemical plants, various other industries, and downtown commercial activities. At most locations, two or three samples were taken on different days, and at a few locations, eight samples were taken on as many different days. Examination of the chromatograms of these samples suggested that more useful results might have been obtained if fewer sites had been used and more samples had been taken at each site. That procedure probably would have permitted a more specific characterization of the nature of the pollution pattern at a given site. Table I lists the sampling sites and includes a column showing the number of different peaks — each corresponding to one compound — that appeared on the chromatograms of the samples from each site.

The chromatograms varied widely in numbers of peaks, areas under the peaks, and in the general patterns of retention times. Figures 2 and 3 show typical chromatograms. In general, the chromatograms of multiple samples from one location did not display a characteristic pattern of peaks. A sample taken on one day was always different from a sample taken on another day at the same site. However, the maximum number of samples from any site was eight, and if it had been possible to obtain a larger number of samples from a given site, it is possible that characteristic patterns might have emerged. Although the objective of establishing characteristic patterns was not achieved, it was shown that the sampling technique was capable of concentrating many compounds from a small volume of air in amounts sufficient for detection and tentative identification.

Samples from sites where automobile traffic was heaviest usually had the most components. Samples taken near iron and steel manufacturing plants usually had few components. The

Table I. Identification of Sampling Sites in the Birmingham Area

Site No.	Location	Most characteristic feature of area	Number of samples taken	Number of different compounds in samples
1	Graymont Avenue at Fifth Avenue North	heavy automobile traffic	2	26
2	Tallapoosa Street at 14th Avenue North	iron foundry	2	16
3	First Avenue North at 24th Street	coffee-roasting plant	8	33
4	Third Avenue South between 35th and 22nd Streets	commercial business	2	12
5	Valley Road	steel mill	1	9
6	Tenth Avenue North at 30th Street	railroad yards	3	21
7	Avenue F, Ensley	near steel mill	2	[illegible]
8	Woodward	steel mill	2	0
9	21st Street at Ninth Avenue South	automobile traffic	2	30
10	19th Street near Sixth Avenue South	automobile traffic	[illegible]	17
11	24th Street at Eighth Avenue North	bedding manufacturer	2	23
12	21st Street Viaduct	near railroad yards	2	0
13	Second Avenue North	downtown business area	2	10
14	First Avenue North Viaduct	automobile traffic	8	23
15	Vanderbilt Road at Norwood Boulevard	iron foundry	8	22
16	19th Street at Eleventh Avenue North	commerical business	2	17
17	50th Street at Division Avenue	steel mill	4	20

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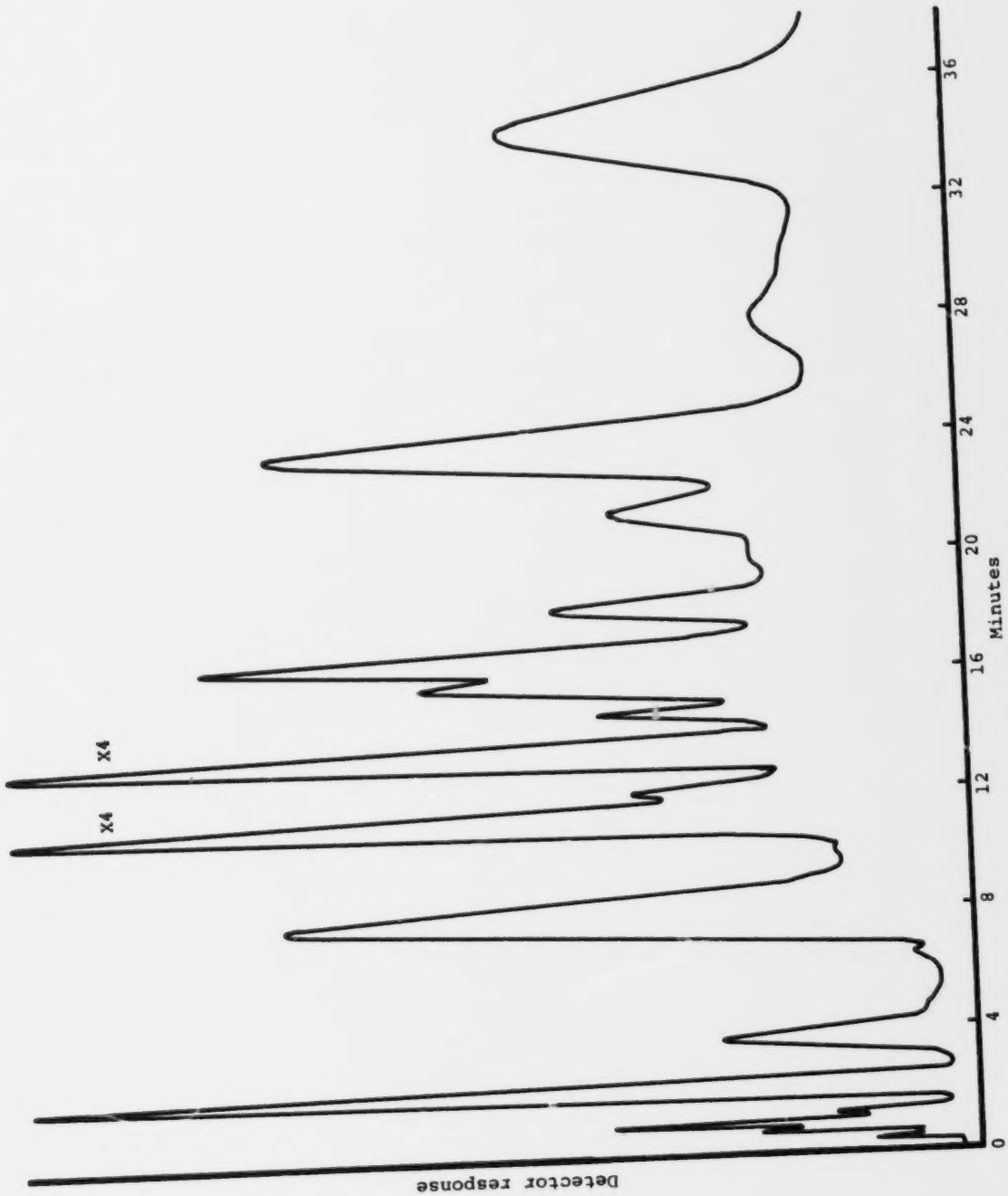

Figure 2. Typical Chromatogram of Sample from Site Characterized by Heavy Automobile Traffic

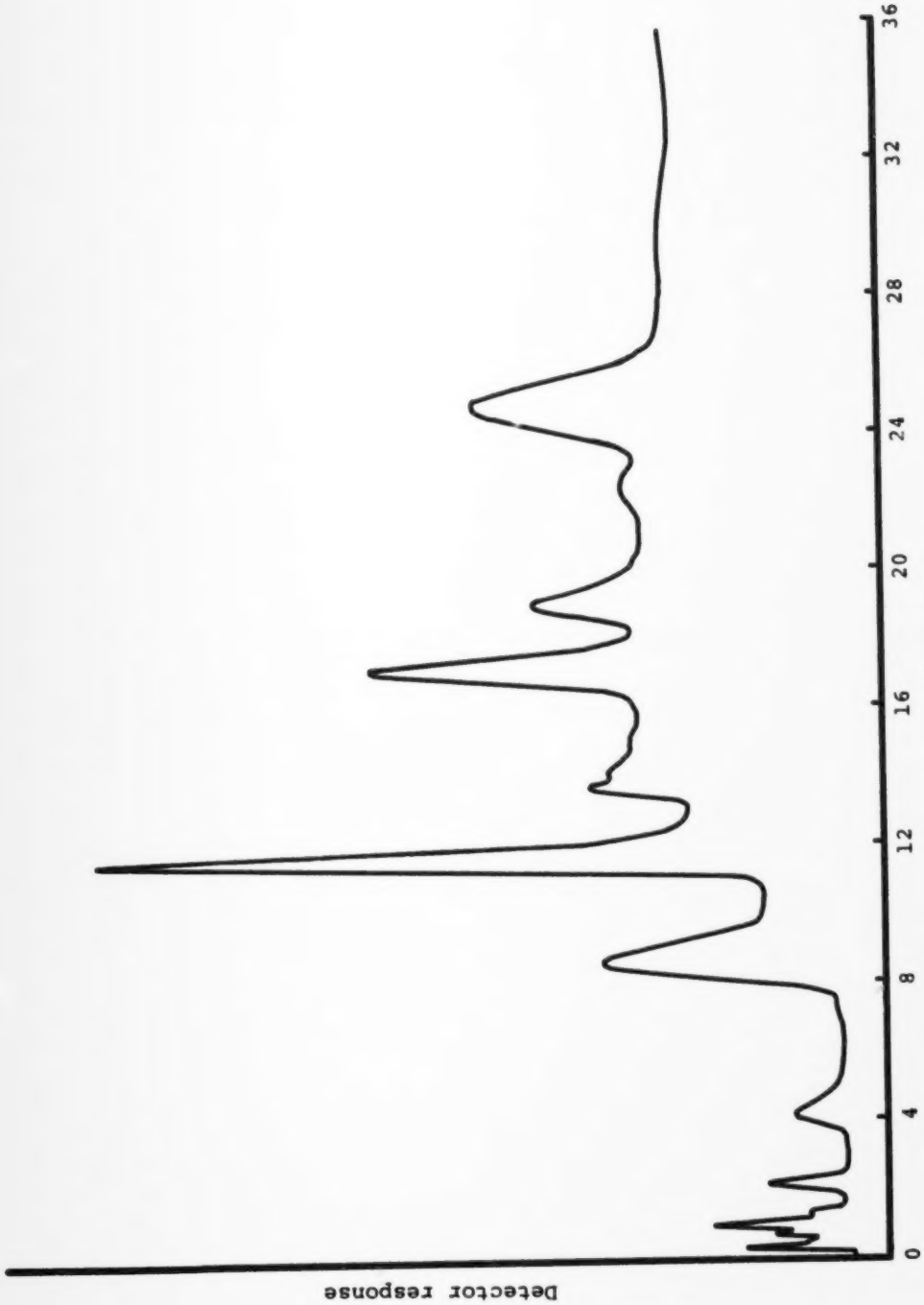

Figure 3. Typical Chromatogram of Sample from a Downtown Site

maximum number of different components detected at one site was 33. That site was near a coffee-roasting plant. Two samples at each of two sites had no peaks at all, apparently indicating a very low degree of organic pollution at the times these samples were collected.

It was necessary to depend upon chromatographic retention times for tentative identification of compounds. The retention times of approximately 50 known organic compounds on the columns used for analysis were carefully determined. These compounds all had retention times within the range of those detected in the atmospheric samples. A few hydrocarbons were included among the "known" compounds. However, on the basis of the experiments described in Section II.B. showing that hydrocarbons were not strongly retained by the sampling loops, it is believed that they could account for only a small proportion of the total amount of substances present in the samples.

Table II lists the specific compounds that were tentatively identified in the various samples. The identifications of seven aldehydes and four alcohols that are based on retention times on two or more different columns are believed to be fairly certain. However, for all other compounds listed it can be said only that the samples contained substances having the same retention times as these compounds. Their identification is uncertain. Only one aromatic compound, benzaldehyde, is in this list. The compounds that appeared to be most widely distributed were ethanol, 1-butanol, 1-pentanol, 1-hexanol, acrolein, methyl acetate, and benzaldehyde. The absence of a compound from the list does not necessarily mean that it was not present in any of the samples. Obviously, the total number of possible organic compounds within the volatility range of the standards is much larger than the number of compounds that were used as standards.

Because of the variations in the amounts of materials collected on the sample loops, quantitative determinations were not possible. However, by comparing peak heights for sample components with peak heights for known amounts of compounds such as acetone, an approximation of the sensitivity limit of the sampling method was obtained. With the procedure described in Section III, the estimated smallest concentration that was detected was 5 ng/l. or approximately 1 part per billion in the 1000 ml of air that was pulled through the sample loop. A peak of average height on the chromatograms represented about 100 ng/l.

Table II. Compounds Tentatively Identified in Air Samples

Compounds identified from retention times on two or more columns	Compounds suggested by retention time on only one column	Number of sampling sites at which compound appeared
Alcohols		
	Methanol	3
Ethanol		5
2-Propanol		4
1-Butanol		11
1-Pentanol		7
	1-Hexanol	7
	1-Octanol	1
	2-Methylcyclohexanol	6
Aldehydes		
Formaldehyde		6
Propionaldehyde		4
Butyraldehyde		5
Valeraldehyde		2
Heptanal		5
2-Ethylbutyraldehyde		7
Acrolein		8
	Benzaldehyde	7
Ketones		
	Acetone	1
Butanone		9
	2-Pentanone	3
	2-Heptanone	4
	2-Octanone	2
	Cyclopentanone	5
	Cyclohexanone	2
Acids		
	Formic	2
	Acetic	1
Esters		
	Methyl acetate	8
	Ethyl acetate	5
	Butyl acetate	7
	Amyl acetate	2
	Methyl acrylate	3

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